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Theoretical Study on the Electronic Structures of Small Ti_nN_m (n + m = 5, 6) Clusters①

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ABSTRACT 45 isomers of Ti_nN_m (n + m = 5, 6) clusters, including linear, some planar and some stero configurations, have been predicted by density functional theory method. For five-atom clusters Ti_3N_2 and Ti_2N_3, the most stable structures are trigonal bipyramid in D_{3h} symmetry, and for Ti_4N cluster, the isomer with one nitrogen atom occupying the center of quasi-tetrahedron is the most stable. In the isomers of Ti_4N_2 and Ti_3N_3, the planar networks are more stable, but for Ti_2N_4, the six-membered ring configuration is the most favorable. Most linear structures can form weak-strong bonds alternately with higher energy. As regards to planar structures, the more Ti–N bonds are formed, the more stable they will be; for stero closed polyhedral isomers, their energies are lower.

Keywords: Ti_nN_m, cluster, quantum chemical study

1 INTRODUCTION

Amorphous alloys comprised of transition metal and non-metal exhibit some interesting properties (such as high conductivity, strong magnetism, corrosion resistance and so on) and have been extensively applied in high-tech fields[1, 2]. Their structures are short-range order and long-range disorder, and are thermodynamically metastable. Up to now, no universal method for their microstructure research has been proposed. However, cluster study with quantum chemical method can provide some useful information on their amorphous structures[3].

Based on a series of studies on some dual-number clusters comprised of early and late transition metals, such as Ti–Ni, Zr–Ni, V–Co, Nb–Co and so on, we found alternative weak-strong localized bond in linear structures as well as some planar structures, and delocalized metallic bond in other structures. Transition metal Ti and non-metal N in this paper can form another kind of amorphous material. Experimental chemists found that Ti_nN_m analogy clusters are fairly stable by using time-of-flight mass spectrometer[4, 5]. Some researchers only made studies on cubic isomers[6]. We also have ever made study on n + m < 4 clusters[7]. Herein, we try to predict the geometric configurations of small Ti_nN_m clusters (n + m = 5, 6) with theoretical calculations and disclose their electronic structures.

2 COMPUTATIONAL DETAILS

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All calculations were performed using the Gaussian program with the hybrid density-functional B3LYP method. The standard 6-31G(d) basis set for N and the small-core RECP (relativistic effective core potential) plus valence double-ζ basis set (LanL2DZ) for Ti were employed. The possible isomer geometries were optimized without constraints on freedom. Reported stationary points have been confirmed to be local minima or transition states by harmonic vibrational analyses at the same level.

3 RESULTS AND DISCUSSION

(1) Five-atom cluster

For five-atom clusters, Ti_2N_3 and Ti_3N_2 are firstly discussed. Nine possible isomers for the Ti_2N_3 clusters have been optimized (all the conformations are verified to be positive by vibration frequency analysis, and the same calculation is carried out on the following optimized isomers). In these nine isomers, three are linear (Fig. 1c). For isomer (1), charges overlap population values are 0.118, 0.671, 0.05 and 0.475 from left to right, respectively, and obviously they are alternatively weak-strong with higher energy. Three N atoms of isomer (2) are located at the center, and stronger bonding can be observed among them but they weakly bond with Ti. Consequently, energy of this isomer is greatly lower than that of isomer (1) (Table 1). In linear isomer (3), Ti locates at the center. It connects with N–N and terminal N–Ti. There is very strong bonding for N–N with charge population being fairly great at the Ti–N. As expected, strong bonding is observed. This isomer is the energetically lowest in linear isomers. Ti_2N_3 has another two chain isomers (4) and (5). For isomer (4), their N–N bond is strong and N–Ti is weak, while Ti–N bond is strong and N–Ti is weak, so weak and strong bonds appear alternatively. Isomer (5) is completely comprised by N–Ti bonds and also exhibits strong-weak-weak-strong bonding. In these nine isomers, bypyramid isomer (9) is the most stable with structural parameters as follows: bond length of Ti–N: 0.228 nm, charges overlap population: 0.239, and bond length of Ti–Ti: 0.185 nm (implying a weak bonding with charge population to be 0.136). No bonding can be found among the three N atoms. Therefore, system energy is the lowest (–280.3982), with higher occurrence probability. Isomers of linear and chain structures have higher energy, and could only exist in excitation state.

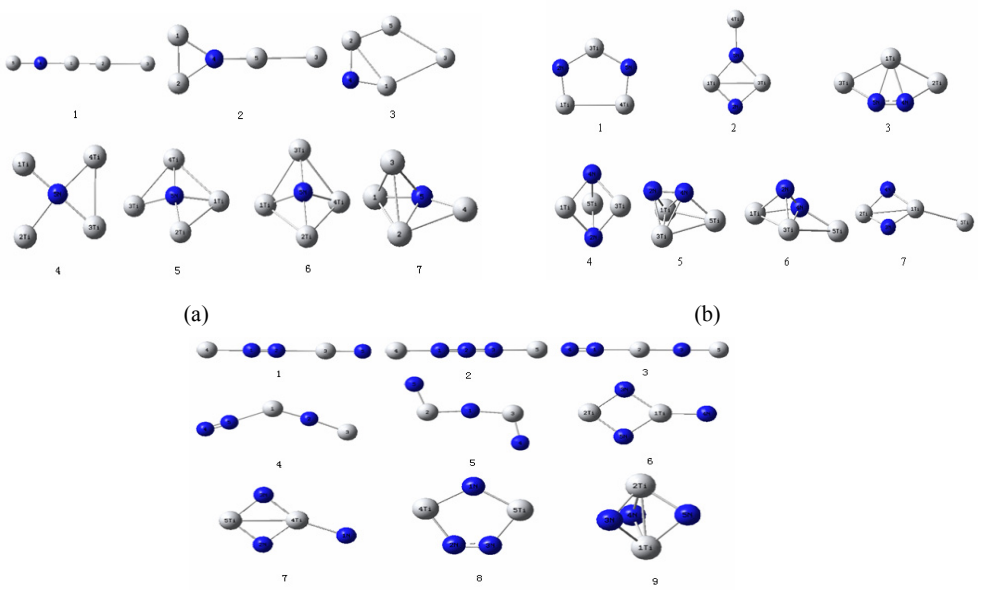


Fig. 1. Prediction of the possible isomers for Ti_4N (a), Ti_3N_2 (b) and Ti_2N_3 (c)

Table 1. Energies of Isomers for Ti_4N, Ti_2N_3 and Ti_3N_2

Ti_4N	2s+1	Sym.	E/a.u. (ΔE/eV)	Ti_3N_2	2s+1	Sym.	E/a.u. (ΔE/eV)	Ti_2N_3	2s+1	Sym.	E/a.u. (ΔE/eV)
1	6	$C_{\infty v}$	–286.7881 (3.555)	1	5	C_1	–283.6997 (0.4053)	1	4	$C_{\infty v}$	–280.1414 (6.985)
2	4	C_{2v}	–286.8538 (1.768)	2	3	C_s	–283.6214 (2.535)	2	4	$C_{\infty v}$	–280.2062 (5.219)
3	6	C_s	–286.8610 (1.5722)	3	1	C_s	–283.5624 (4.140)	3	4	$C_{\infty v}$	–280.3340 (1.746)
4	4	C_s	–286.8975 (0.5794)	4	1	D_{3h}	–283.7146 (0.00)	4	2	C_s	–280.3239 (2.021)
5	4	C_1	–286.9167 (0.0571)	5	1	C_s	–283.5997 (3.125)	5	2	C_1	–280.2904 (2.932)
6	4	C_1	–286.9173 (0.0408)	6	5	C_1	–283.6051 (2.978)	6	2	C_{2v}	–280.1798 (5.940)
7	4	C_1	–286.9188 (0.00)	7	5	Cs	–283.5936 (3.291)	7	6	Cs	–280.2635 (3.664)
								8	6	C_{2v}	–280.2444 (4.183)
								9	2	D_{3h}	–280.3982 (0.00)

For Ti_3N_2 clusters, 7 possible isomers could be obtained, among which bypyramid isomer (4) is also the most stable with charges overlap populations of Ti–N and Ti–Ti being 0.156 and 0.008, respectively. Charges overlap populations indicate a Ti–N chemical bond and weak Ti–Ti bond. The same condition can be seen in the most stable isomer (9) of Ti_2N_3. There is no bonding for N–N, and each N atom could gain 0.842 electrons and each Ti atom could provide 0.562 electrons. The isomer with the second lowest energy is a five-membered ring isomer (1) with crossing layout of Ti–N. Its energy is only 0.405 eV higher than that of bypyramid isomer. Charges overlap population for the Ti–N bond reaches 0.22~0.34. There is weak bonding of 0.007 for Ti–Ti bond. These two isomers have higher occurrence probability. Sector isomer (3) has fairly higher energy. The N–N is linked, and Ti–N shows strong-weak-weak-strong bonding. Charges overlap population for weak Ti–N bond is only 0.089 and the bond length is as long as 0.202 nm, so this isomer has the highest energy.

Seven isomers are optimized for Ti_4N. Energies of cubic isomers of (5), (6) and (7) are very similar, all of which are quasi-tetrahedrally coordinated with one N atom and four Ti atoms. N could basically gain 1.0 electron. Each of four Ti atoms in isomer (5) could provide 0.25 electrons averagely. For isomers (6) and (7), some Ti could provide 0.4 electrons, and some others could only denote 0.12~0.13 electrons. These several isomers have fairly low energy and higher occurrence possibility. For linear structure, there are two Ti–Ti bonds with the one in the middle being stronger than that at side. One of Ti–N bonds is strong, and the other is weak. Their charges overlap populations (from left to right) are 0.323, 0.273, 0.358 and 0.219, respectively. Isomer (2) shows T-shape. Compared with linear structure, its two Ti–Ti bonds are stronger and Ti–N strong-weak. Owing to the lots of bonds, its energy is lower than that of linear structure.

We have also tried to search TiN_4 clusters, but no stable isomer is obtained.

(2) Six-atom cluster

Two linear, three planar and five three-dimensional isomers are obtained through the optimization of Ti_4N_2 clusters (Fig. 2). Among them, planar isomer (3) has the lowest energy and the greatest occurrence probability (Table 2). In this isomer, each N atom coordinates to 3 Ti atoms and 0.939 electrons are obtained in total. Two Ti atoms lose 0.23 electrons, and the other two Ti lose 0.66~0.74 electrons. For

planar isomers (4) and (5), each N atom obtains 0.6 electrons. However, Ti atoms are different. For isomer (4), Ti atoms lose charges of 0.153 and 0.447, respectively. For isomer (5), Ti atoms lose charges of 0.369 and 0.827, respectively, and another Ti atom obtains 0.229 charges. Linear isomers (1) and (2) exhibit bonding in an alternatively strong-weak layout, with energy 8~9 eV higher than that of isomer (3) and less occurrence probability. Cubic isomer (8) shows distorted octahedron with higher symmetry of D_{4h}. Bond length of N–N is 0.149 nm, and that of Ti–N 0.201 nm. According to the analysis of charge population, it could be found that the Ti–Ti bond is stronger, while N–N and Ti–N are weaker, so the energy is higher. For isomer (9), four Ti atoms show diamond shape and are nested with diamond comprised of two Ti atoms and two N atoms. N–N is separated entirely, Ti–Ti is fairly weaker, and Ti–N is stronger, so it has the lowest energy in cubic isomers with total energy only 1 eV higher than that of planar isomer (3).

Table 2. Electronic Properties of Possible Isomers for Ti_4N_2

No.	2s+1	Sym.	E/a.u.	Mulliken over. pop.			Atomic charges		Freq./cm^{-1}
			(ΔE/eV)	Ti-Ti	Ti-N	N-N	Ti	N	
1	3	$D_{\infty h}$	–341.4152	0.234	0.299	0.289	0.326	–0.335	3.3, 4.6, 5.1(2),95.7, 30.9,
			(9.541)				0.008		162.3(2),368.4(2), 380.4,
									837.2, 1443.6
2	1	$C_{\infty V}$	–341.4511	0.126,	0.006,	0.354	0.154,	–0.210	6.3(2), 61.8(2),91.0(2),94.3,
			(8.565)	0.544	0.301		0.076,	–0.396	333.3(2),353.9,548.5,863.0,
							0.456		1444.5
3	5	C_1	–341.7660	0.247,	0.151,		0.232,	–0.939	8.5, 25.2, 87.1,134.0,153.7,
			(0.00)	0.293	0.230		0.746		212.7,303.8,347.8,458.2,
							0.663,		474.6,767.4,890.2
4	1	C_{2h}	–341.6683	0.133	0.310		0.447	–0.600	65.8,75.5,157.4,250.6,275.2
			(2.657)	0.240	0.306		0.153		300.4,353.5,443.6,642.8,
									707.3,779.9,790.0
5	1	C_{2v}	–341.6860	0.372	0.280		0.827,	–0.668	42.3,125.3,180.7，211.0,
			(2.176)		0.314		–0.229		345.0,356.0，375.9,460.2,
							0.369		570.1,653.9,770.4,928.0
6	1	C_{2v}	–341.6443	0.208	0.034–		0.428	–0.558	168.1,174.1,183.7,208.8,
			(3.310)	0.171	0.134		0.131		290.7,358.3,365.2,374.0,
				0.170	0.356				508.4,536.3,601.9,1243.3
7	1	C_{2v}	–341.6153	0.695	0.204	0.028	0.138	–0.486	96.4,150.5,153.5,161.5,
			(4.099)	0.019			0.348		164.1,280.5,407.6,415.6,
				0.078					525.9,40.6,583.8,910.2
8	3	D_{4h}	–341.5961	0.256	0.027	0.192	0.375	–0.750	24.6,151.0,156.0,165.9,
			(4.621)						229.2,328.9,405.9,464.8,
									471.4,532.8,547.7,898.0
9	1	C_{2v}	–341.7287	0.067	0.205		0.433	–0.824	73.8,92.2,181.9,304.3,
			(1.015)		0.305		0.440	–0.921	316.2,321.3,411.0,415.5,
									424.4,632.6,646.7,775.5
10	1	C_1	–341.6512	0.411	0.190	0.038	0.214,	–0.503	151.6,189.0,205.2,269.7,
			(3.123)	0.044	0.073		0.565,	–0.782	302.9,318.5,348.2,425.6,
				0.241	0.291		0.109		538.0,589.2,662.5,770.3

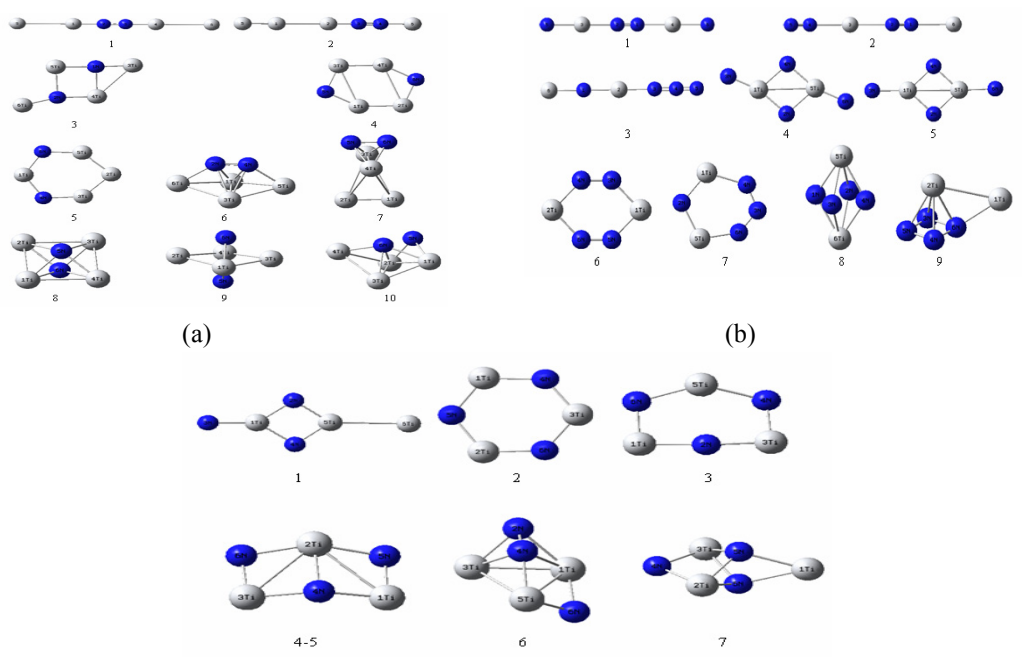
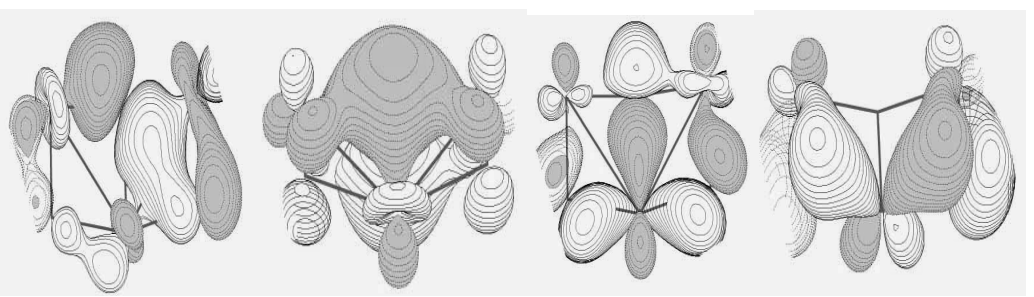


Fig. 2. Prediction of the possible isomers for Ti_4N_2(a), Ti_2N_4 (b) and Ti_3N_3 (c)

Three linear isomers with different spin multiplicity are obtained after optimizing cluster Ti_2N_4. For isomer (1), tri- and five-spin multiplicity opposes weak Ti–N bonds. Thus its energy is high and occurrence probability is nearly zero (Table 3). Isomers (2) and (3) also have higher energy. For isomer (3), energy of five-spin multiplicity is 3.79 eV higher than that of isomer (7) with the lowest energy. For four planar isomers of Ti_2N_4, both isomers (4) and (5) consist of two Ti and two N atoms to give a tetrahedron and link with two Ti atoms. In addition, for two planar six-membered isomers, isomer (6) has Ti–N and N–N bonds with stronger bonding, so this structure is energetically lower and stable. For isomer (7), charge populations of N–N and Ti–N bonds are 0.264~0.334 and 0.246~0.296, respectively with strong bonding, and therefore its total energy is the lowest among the nine isomers with the greatest occurrence probability. Cubic isomer (8) has D_{4h} symmetry. There is nearly no bonding for N–N, and only weak bonding for Ti–N, so its energy is fairly higher. Isomer (9) has poor symmetry with plenty of Ti–N bonds, and then its energy is similar to that of isomer (8).



No.20 No.21 No.22 No.24

Fig. 3. Some bonding orbitals of isomer 4 for Ti_3N_3

Table 3. Electronic Properties of Possible Isomers for Ti_2N_4

No.	2s+1	Point group	E/a.u. (ΔE/eV)	Over.pop. Ti–Ti	Over.pop. Ti–N	Over.pop. N–N	Atomic charges Ti	Atomic charges N	Freq./cm^{-1}
1	3	$D_{\infty h}$	–334.6215 (12.857)		0.106 –0.213	0.686	0.579	–0.199 –0.380	31.5,32.2,69.8, 96.2,123.2, 166.9,235.3,246.4,306.8, 355.4,594.7,785.3,2029.4
	5	$D_{\infty h}$	–334.6701 (11.538)		0.151–0.175	0.615	0.549	–0.235 –0.314	39.2(2)93.5(2),199.9,219.2(2)365.3,365.3,429.0,520.4, 570.4,1877.0
2	1	$C_{\infty v}$	–334.8540 (6.533)		0.005–0.007	0.729–0.889	–0.149 –0.077	0.053 0.077 0.030	46.1,46.4,79.7,104.2,104.8, 153.1,211.0,222.8,223.8, 255.6,400.0,2489.3,2511.9
3	3	$C_{\infty v}$	–334.8470 (6.724)		0.087–0.209	0.524–0.603	0.591 0.320	–0.474 –0.514 0.348 –0.270	17.0,18.5,78.6,85.0,140.4, 147.9,182.4,412.9,541.1, 617.4,617.5,1459.0,2256.1
	5	$C_{\infty v}$	–334.9547 (3.794)		0.185–0.226	0.555–0.598	0.847 0.323	–0.709 –0.530 0.332 –0.263	16.7,17.1,69.2,89.2,131.2, 146.1,263.8,453.9,623.1, 626.1,851.8,1456.4,2272.4
4	1	C_{2h}	–334.9219 (4.687)	0.219	0.222 0.432 0.169		0.822	–0.572 –0.250	64.6,170.0,176.1,202.6,250.3, 283.7,473.4,603.4,713.1, 722.1,930.2
5	3	C_s	–334.960 (3.650)	0.225	0.223 0.256		0.936 0.945	–0.627 –0.313 –0.636	100.0,106.8,107.5,163.7, 268.3,374.6,434.8,579.8, 620.8,774.4,797.2,826.0
	5	C_{2v}	–334.9067 (5.100)	0.239	0.216 0.222		0.932	–0.612 –0.320	78.4,107.8,111.5,130.6, 280.4,309.3,313.4,548.6, 577.4,622.0,628.2,791.5
6	1	D_{2h}	–335.0801 (0.3835)		0.388	0.261	0.693	–0.346	188.2,339.0,346.8,377.4, 388.2,591.5,599.2,664.6, 729.0,888.1,1164.2,1244.3
7	3	C_s	–335.0942 (0.00)		0.246 0.296	0.264 0.334	0.842 0.678	–0.725 0.056 –0.434	109.6,104.8,214.7,266.9, 292.9,493.5,584.3,662.0, 754.8,792.7,1102.4,1313.9
8	5	D_{4h}	–334.9450 (4.058)		0.069	0.005	0.719	–0.359	252.2(2),340.1(2),359.8, 405.5,483.6,729.9(2),836.6, 880.9,892.3
9	5	C_1	–334.9646 (4.031)	0.272	0.123，–0.131	0.180–0.183	0.299 0.592	–0.160 –0.163 –0.407	109.6,147.9,294.4,325.4, 360.8,461.3,736.0,893.9, 939.9,1128.4,1151.8,1209.7

Table 4. Geometric and Electronic Properties of Possible Isomers for Ti_3N_3

No.	2s+1	Sym.	E/a.u.	Bond length/nm Ti–Ti	Bond length/nm Ti–N	Bond length/nm N–N	Over.pop. Ti–Ti	Over.pop. Ti–N	Over.pop. N–N	Atomic charges Ti	Atomic charges N
1	2	C_s	–338.1395	0.287	0.184–0.187		0.264	0.220–		0.833	–0.648
				0.307	0.192		0.246	0.237		0.502	–0.355
										0.317	–0.650
2	4	C_s	–338.5217		0.178–0.184			0.266–		0.807	–0.736
								0.302		0.622	–0.764

3	6	C_1	–338.4588		0.172–0.198			0.155–		0.652~	–0.809~
								0.355		0.806	–0.645
4	2	C_1	–338.5607	0.272	0.172		0.032–	0.157–		0.623~	–0.951~
					0.191–0.199		0.063	0.380		1.048	–0.662
5	4	C_s	–338.5583	0.272	0.172		0.056–	0.377–		0.610	–0.955
					0.187–0.199		0.058	0.159		1.070	–0.667
6	2	C_1	–338.4672	0.253–	0.190–0.212	0.137	0.185	0.061–		0.728	–0.483
				0.263	0.188		0.096	0.362		0.560	–0.630
					0.175		0.088			0.478	–0.652
7	6	C_{2v}	–338.1918		0.197–0.203	0.149		0.069–	0.128	0.378	–0.515
					0.211			0.145		0.713	–0.645

Six isomers are obtained for the optimization of Ti_3N_3 with isomer (4) exhibiting the lowest energy. According to its molecular orbital graph (Fig. 3), we find that: except 18 inner orbitals with lower energy, No. 19 (2*p* orbitals of N in the middle) and No. 20 orbitals (adjacent 3*d* and 4*s* orbitals of Ti) form the bonding orbitals. Orbital No. 21 is a large π bond comprised by 2*p* orbitals in three N atoms and 3*d* orbitals in three Ti atoms. Orbitals No. 22~27 are bonding orbitals consisting of 3*d* orbital of Ti and 2*p* orbital of N. Orbitals No. 28 and 29 are non-bonding orbitals of two Ti atoms. Isomer (2) has the lowest energy with Ti and N crossing all Ti–N stronger bonds. Each Ti atom could provide 0.622～0.807 charges, and each N atom could obtain 0.73～0.76 charges. It has the total energy 1 eV higher than that of isomer (4) with greater occurrence probability.

4 CONCLUSION

According to the isomers search of Ti_nN_m clusters, we found that when the number of Ti atoms is more than that of N atoms, structures with N atoms in a separate layout are energetically lower, but when the situation is on the contrary, the isomer with direct N–N bond is energetically more favorable. Isomers with less atoms and high symmetry (such as Ti_3N_2 and Ti_2N_3) have the lowest energy. When the number of atoms increases, planar isomers (such as Ti_4N_2 and Ti_2N_4) or quasi-planar isomer (such as Ti_3N_3) are the most stable.

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